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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: MANGANESE - 1968

C. V. Spangler

W. E. Davis and Associates

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NATIONAL INVENTORY OF SOURCES AND EMISSIONS: MANGANESE - 1968

by

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9726 Sagamore Road
Leawood, Kansas

Contract No. CPA-70-128

EPA Project Officer: C. V. Spangler

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Publication No. APTD-1509

PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. CPA 70-128 with the Environmental Protection Agency, Office of Air Programs.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of the emissions of manganese in the United States for the year 1968.

Background information concerning the basic characteristics of the manganese industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact about fifteen percent of the companies in each major emission source group to obtain the required information. It was known that published data concerning emissions of the pollutant was virtually nonexistent, and contacts with industry ascertained that atmospheric emissions were not a matter of record.

The manganese emissions and emission factors presented are based on the summation of information obtained from manufacturing companies that represent approximately eighty percent of the total production, and reprocessing companies that handle about thirty percent of the manganese used in consumer products. Air pollution control equipment is in use at many of the manganese reprocessing facilities, but its use at processing plants is limited.

Manganese emissions and emission factors are considered to be reasonably accurate.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the manganese industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal and State Governments.

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The inventory of atmospheric emissions has been prepared to determine the nature, magnitude, and extent of the emissions of manganese in the United States for the year 1968. The flow of manganese in the U. S. for that year has been traced and charted. The consumption was 1,150,000 tons while domestic production was only 48,000 tons. Imports principally from Brazil, Gabon, Republic of South Africa, Congo, Guyana, India, Angola, and Australia totaled 1,053,000 tons. Emissions to the atmosphere during the year were 18,992 tons. About 47% of the emissions resulted from the production of ferroalloys and about 37% from the production of iron and steel. The combustion of coal was also a significant source of manganese emissions.

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SUMMARY

The flow of manganese in the United States has been traced and charted for the year 1968. The consumption was 1,150,000 tons while domestic production was only 48,000 tons. Imports principally from Brazil, Gabon, Republic of South Africa, Congo, Guyana, India, Angola, and Australia totaled 1,053,000 tons.

Emissions to the atmosphere during the year were 18,992 tons. About 47 percent of the emissions resulted from the production of ferroalloys and about 37 percent from the production of iron and steel. The combustion of coal was also a significant source of manganese emissions.

Emission estimates for mining, production of manganese metal, and reprocessing operations are based on data obtained by personal contact with processing and reprocessing companies.

EMISSIONS BY SOURCE
1968

Source Category	Source Group	Short Tons	
Mining			5
Processing			9,271
	Manganese Metal	325	
	Manganese Alloys	8,946	
Reprocessing			7,584
	Carbon Steel	4,340	
	Cast Iron	2,770	
	Welding Rods	24	
	Nonferrous Alloys	60	
	Batteries	90	
	Chemicals	300	
Consumptive Uses			1,957
	Coal	1,950	
	Oil	7	
Incineration and Other Disposal			175
	Sewage and Sludge	175	
TOTAL			18,992

EMISSION FACTORS

Mining	0.2 lb/ton of manganese mined
Processing	
Manganese Metal	25.0 lb/ton of manganese processed
Ferromanganese	
Blast Furnace	4.1 lb/ton of ferromanganese produced
Electric Furnace	23.9 lb/ton of ferromanganese produced
Silicomanganese	
Electric Furnace	69.4 lb/ton of silicomanganese produced
Reprocessing	
Carbon Steel	
Blast Furnace	22.5 lb/1,000 tons of pig iron produced
Open-Hearth Furnace	51 lb/1,000 tons of steel produced
Basic Oxygen Furnace	44 lb/1,000 tons of steel produced
Electric Furnace	78 lb/1,000 tons of steel produced
Cast Iron	330 lb/1,000 tons of cast iron
Welding Rods	16 lb/ton of manganese processed
Nonferrous Alloys	12 lb/ton of manganese processed
Batteries	10 lb/ton of manganese processed
Chemicals	10 lb/ton of manganese processed
Consumptive Uses	
Coal	7.7 lb/1,000 tons of coal burned

SOURCES OF MANGANESE

Manganese is a hard and very brittle metal that melts at 1,260 C. Its atomic weight is 54.93 and its specific gravity is 7.4. It is a relatively abundant element present in varying quantities in about ninety-five percent of the earth's crust. Ore deposits of commercial importance are found throughout the world. The most important manganese-producing countries are Australia, Brazil, China, Gabon, Ghana, India, the Republic of South Africa, and the U.S.S.R.

The most common manganese minerals are pyrolusite, psilomelane, braunite, hausmannite, rhodonite, and rhodochrosite. They range in color from red to brown and black, containing from forty to seventy percent manganese.

In the United States ores containing manganese are found in Arizona, Arkansas, Colorado, Maine, Montana, Minnesota, New Mexico, and South Dakota. Most of the ore mined in these states is manganiferous ore (5 to 35 percent Mn content). The United States is largely self-sufficient with respect to its use of manganiferous ore, but is almost entirely dependent on other countries for manganese ore (35 percent or more Mn content).

Manganese is also commonly found associated with iron ores, usually in concentrations too low to make its commercial recovery economically feasible.

MANGANESE

MATERIAL FLOW CHART - 1968

Short Tons - Mn Content

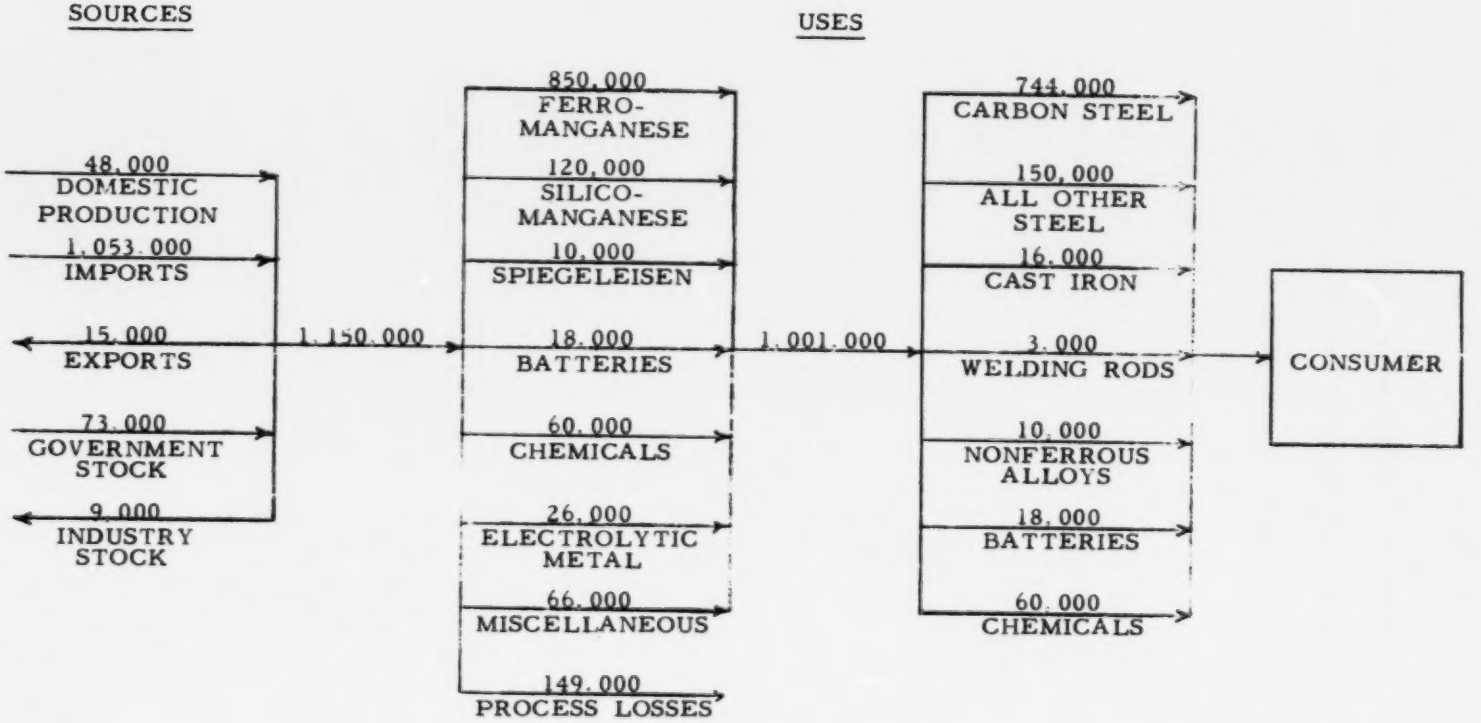

Figure 1

MATERIAL FLOW

MINING

Manganese produced in the United States during 1968 was approximately 4 percent of the manganese consumed. Manganese ore (35 percent or more Mn) was produced and shipped from Montana and New Mexico. Manganiferous ore (5 to 35 percent Mn) was produced and shipped from Colorado, Minnesota, Montana, and New Mexico.

MANGANESE PRODUCTION IN UNITED STATES [1]/
1968

	Manganese Content Short Tons
Manganese Ore	6,000
Manganiferous Ore	42,000
Total	48,000

1- Personal Communication: U. S. Department of Interior; Bureau of Mines; August, 1970.

IMPORTS AND EXPORTS

During 1968 imports of manganese ore were principally from Brazil, the Congo, Gabon, Ghana, India, and the Republic of South Africa. The imports of manganese ore totaled 1,831,210 short tons (gross weight), silicomanganese imports for consumption were 25,142 short tons (gross weight), and ferromanganese imports were 207,677 short tons (gross weight) [1]. The manganese content of the imports was 1,053,000 short tons [2].

Exports of all forms of manganese during 1968 were 15,000 short tons (Mn content) [2] including ferromanganese, manganese and manganese alloys, waste and scrap, ore, and concentrates containing more than 10 percent manganese.

MANGANESE STOCKS

During 1968 industry stocks of manganese in all forms increased 9,000 short tons (Mn content), while government stocks decreased 73,000 short tons (Mn content) [2].

1- Minerals Yearbook; Bureau of Mines; 1968.

2- Personal communication; U. S. Department of Interior; Bureau of Mines; August, 1970.

PROCESSING

The chief use of manganese ore (35 percent or more Mn) in the United States is in the production of manganese metal, ferromanganese, silicomanganese, and spiegeleisen. These products are used principally in the iron and steel industry.

Other important uses of smaller quantities of the ore include its use in the manufacture of chemicals, batteries, welding rods and nonferrous alloys.

During 1968, manganese ore was used in the manner shown in Table I.

TABLE I

USES OF MANGANESE ORE [1]/
1968

Use	Short Tons Mn Content
Manganese Metal (electrolytic)	26,000
Ferromanganese	850,000
Silicomanganese	120,000
Spiegeleisen	10,000
Chemical Manufacture	60,000
Battery Manufacture	18,000
Miscellaneous	66,000

1- Personal communication; U. S. Department of Interior; Bureau of Mines; August, 1970.

REPROCESSING

In the United States the principal use of manganese is in the production of carbon and alloy steels. Metallurgically, it is used chiefly as ferromanganese and to a lesser extent in the forms of silicomanganese, spiegeleisen and manganese metal. For battery manufacture, it is used in the form of manganese dioxide.

In the chemical industry, manganese is used as an oxidizing agent in the manufacture of hydroquinone and for the production of various chemicals including manganous oxide, manganous chloride, potassium permanganate, and manganese sulfate.

The consumption of manganese in the United States during 1968 has been reported at 1,101,000 short tons [1].

CARBON STEEL

Manganese is used in steelmaking, chiefly to counteract the effects of sulfur; however, it also has other advantages. It has some deoxidizing power and, when added in certain proportions, it can act to harden and reduce the plasticity of steel.

Steels that contain too much sulfur tend to crack during rolling operations; a condition known as "hot shortness". Excess sulfur

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1 - Personal communication; U. S. Department of Interior; Bureau of Mines; October, 1970.

also tends to create surface imperfections during fabrication. The use of manganese in steelmaking effectively prevents these difficulties. Most of the unwanted sulfur combines with the manganese and is carried into the slag.

In the United States the use of manganese in carbon steel during 1968 was 744,000 short tons [1]/.

OTHER STEEL

In addition to its functions in the production of carbon steel, manganese is used as an alloying agent in special steels to produce harder and tougher metals for special applications. In plain carbon steel the manganese content is less than one percent, but in one group of extremely hard and tough alloy steels the manganese content is from 10 to 14 percent.

During 1968, the use of manganese in other steels was 150,000 short tons [2]/.

CAST IRON

The principal use of manganese in the production of cast iron is

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1- Personal communication; U. S. Department of Interior; Bureau of Mines; October, 1970.

2- Personal communication; U. S. Department of Interior; Bureau of Mines; August, 1970.

to nullify the effects of sulfur.

During 1968 the use of manganese in cast iron totaled 16,000 short tons [1].

WELDING RODS

Manganese, in the dioxide form, has important uses in the manufacture of welding rods and welding rod coatings. Its principal use is as an oxidizing agent. The MnO_2 content of typical welding rod coatings is in the order of 11 percent.

During 1968 about 3,000 short tons of manganese were used in the manufacture of welding rods [2].

NONFERROUS ALLOYS

Manganese is important in many miscellaneous metallurgical applications. It is used in the production of aluminum and magnesium and it is alloyed with copper to make manganese bronze. It imparts stiffness and hardness to aluminum and magnesium; manganese also increases the corrosion resistance of magnesium.

The alloy, manganese bronze, is a complex brass. It has hot

1- Personal communication; U. S. Department of Interior; Bureau of Mines; October, 1970.

2- Personal communication; U. S. Department of Interior; Bureau of Mines; August, 1970.

working properties, high strength, and abrasion resistance. It is used extensively for ship propellers, boat shafting and other similar applications.

In the United States, the use of manganese in nonferrous alloys during 1968 was 10,000 short tons [1].

BATTERIES

Synthetic ore is a term used chiefly to identify manganese dioxide that is produced chemically or electrolytically for use in dry cell batteries. The Bureau of Mines define synthetic ore as a material that is the equivalent of, or better than, natural ore, which can be put to the same uses, and is produced by means other than ordinary concentrations, calcining, sintering, or nodulizing.

In batteries, manganese dioxide acts as a depolarizing agent. Hydrogen released from the electrolyte of the cell tends to form around the carbon electrode and slow down the cell action. Oxygen provided by the manganese dioxide corrects this condition by its reaction with the hydrogen.

1- Personal communication; U. S. Department of Interior; Bureau of Mines; October, 1970.

During 1968 manganese used in batteries totaled 18,000 short tons [1].

CHEMICALS

Manganese dioxide ores are important in the manufacture of manganese chemicals, many of which are used as oxidizing agents. Manganese sulfate is used in fertilizers, fertilizer additives, as a constituent of animal and poultry feeds, as a paint drier, as a coloring agent for ceramics and textiles, and as a base for other chemicals. Manganous chloride is used in dyeing textiles, and as a vehicle for alloying manganese with magnesium. Manganous oxide is also used in animal and poultry feeds, fertilizers, and welding applications.

Manganese used in the manufacture of chemicals during 1968 totaled 60,000 short tons [1].

1- Personal communication: U. S. Department of Interior; Bureau of Mines; August, 1970.

EMISSIONS

MINING

Because of the marked differences in the manner in which manganese deposits occur, a wide variety of mining methods are used. In the United States, in recent years, high grade manganese ore has come from underground mines. On the other hand, manganiferous ores are usually mined in the same manner as iron ores from the same district and, in the United States, this has meant open pit mines.

Before 1950, very few of the world's manganese ore producers had milling plants other than simple crushing, screening and washing installations. This was also the situation in the United States, except in the State of Montana where concentrating equipment was used for battery grade ores. Due to the recent high rate of industrial growth more producers have installed various kinds of concentrating equipment, many times including sintering and nodulizing equipment to agglomerate fines and remove deleterious impurities.

While this study was in progress, mining companies were contacted concerning the quantity of ore mined, its manganese content, and the manganese emissions occuring during mining and concentration. It was found that records of manganese emissions to the atmosphere are not maintained. Most of those contacted indicated losses to the

atmosphere are slight, occuring principally during ore handling or crushing and due to wind loss from tailings.

Based on information obtained and observations made during visits to mining locations, the manganese emissions to the atmosphere from sources of mining are estimated at 0.2 pounds per ton of manganese mined. Manganese emissions to the atmosphere during 1968 were 4.8 tons.

PROCESSING

In the United States the principal use of manganese ore (35 percent or more Mn) is in the production of manganese alloys and pure manganese metal.

MANGANESE METAL

The process currently used to produce pure manganese metal is an electrolytic process consisting of four principal steps: roasting of the ore, leaching, purification of the leach liquor, and electrodeposition of the manganese. During roasting the primary object is to convert all manganese to the oxide form and at the same time leave as much iron as possible as Fe_3O_4: however, most ores treated by this process are relatively low in iron and roasting is at a high temperature to achieve maximum recovery of manganese without regard to iron content. When the iron content is low it can be controlled by pH adjustment of the leaching acid.

After grinding and roasting, the ore is leached with anolyte from the electrolytic cell. The concentration of the leach is adjusted by addition of ammonium sulphate to maintain a concentration of about 140 grams/litre, and sulphuric acid to give a pH of about 2.5. After solution, the leach liquor is neutralized to pH 6.5 by adding ammonia, milk of lime, or calcined ore. On neutralization of the leach liquor, iron and aluminum hydroxides are

precipitated. Overall extraction of manganese from the ore is about 98 percent.

The neutral leach liquor contains small quantities of numerous elements, such as arsenic, cobalt, copper, iron, lead, molybdenum, and zinc which must be removed prior to electrolysis. The removal is accomplished by first treating the liquor with hydrogen sulphide or ammonium sulphide, then filtering to remove the sulphides. At this point most of the impurities have been removed except colloidal sulphur and small quantities of arsenic and molybdenum. These are removed by the addition of iron in the form of copperas. The iron is oxidized at room temperature at a pH of 6.5 to 7.0 and ferric hydroxide is precipitated; the arsenic, molybdenum, and colloids are absorbed. At this stage the solution has been purified and is ready for feeding to the electrolytic cell.

The cell consists of an anode compartment and a cathode compartment separated by a diaphragm. The purified solution first enters the cathode compartment, then flows through a canvas diaphragm into the anode compartment and is discharged to a storage tank for reuse. The manganese is deposited at the cathode of the cell.

The principal manganese emissions to the atmosphere that occur are due to handling, grinding, and roasting of the ore. The data obtained regarding two electrolytic plants indicate overall emissions average 25 pounds per ton of manganese processed. In the year 1968 the atmospheric emissions of manganese resulting from the production of manganese metal totaled 325 tons.

MANGANESE ALLOYS

About 85 percent of the manganese ore consumed in the United States during 1968 was used to produce manganese alloys, the greater part of which was in the form of high, medium and low carbon ferromanganese. These and other alloys, including silicomanganese and spiegeleisen, are used principally by the steel industry.

Air pollution controls have not been satisfactory in the ferroalloy industry; thus a more intensive effort will be required in order to provide adequate control of process emissions. There are numerous technical problems that must be solved and the addition of proper fume collection equipment is not the only requirement for a satisfactory long-range solution. There are many dust and fume producing operations. The dust (larger than 2 micron size) that results from raw material handling, as well as that from crushing and sizing of the product, can be handled by conventional techniques; the major pollution problem is associated with the ferroalloy furnaces and the collection of fume that is less than 2 microns in size.

About 65 percent of the ferromanganese is made in blast furnaces and the remaining 35 percent in electric furnaces. The blast furnaces used in making ferromanganese are the same type as those used in making pig iron; quite often the same furnace is

used to produce both products. Ferromanganese is often produced by operating a pig iron furnace on manganese alloy production long enough to obtain a supply of the alloy, after which the blast furnace is returned to its normal operation of producing pig iron.

The effluent from a ferromanganese blast furnace is reported to be a greater air pollution problem than that from an iron blast furnace 1/. It is said to be the most prolific pollution producer of any of the metallurgical processes 2/. One investigator has reported that emissions from ferromanganese blast furnaces, if uncontrolled, are nearly 150 tons of dust per 1,000 tons of metal produced 2/. Another investigator has reported the properties of ferromanganese blast furnace fume as shown in Table II.

Electric furnaces used for making manganese ferroalloys are the same type as those used in making other ferroalloys and, again, the furnace used is not always devoted exclusively to making one particular product. In fact, there is often some interchangeability in scheduling production of the various ferroalloys.

1- Thring, N. W. and Sarjant, R. J.; "Dust Problems of the Iron and Steel Industry"; Iron and Coal Traders Rev.; Vol. 174; Mar. 29, 1957.

2- Wurts, T. C.; "Industrial Sources of Air Pollution - Metallurgical"; PHS Publ. 654; 1959.

TABLE II

PROPERTIES OF PARTICULATE MATTER
FROM A FERROMANGANESE BLAST FURNACE [1]

Component	Content %
Manganese	15 to 25
Iron	0.3 to 0.5
Total alkali (as Na_2O and K_2O)	8 to 15
Silicon dioxide (SiO_2)	9 to 19
Aluminum oxide (Al_2O_3)	3 to 11
Calcium oxide (CaO)	8 to 15
Magnesium oxide (MgO)	4 to 6
Total sulfur (as SO_4)	5 to 7
Carbon	1 to 2
Particle Size (average)	0.3 micron
Apparent Density	12 lb/cu. ft.

1- Bishop, C. A. et al; "Cleaning Ferromanganese Blast Furnace Gas"; Iron Steel Engineer; 28; Aug. 1951.

When using the conventional submerged arc electric furnace to produce manganese alloys, large quantities of carbon monoxide are generated as a result of carbon reduction of metallic oxides. This gas, along with other primary gas due to moisture in the charge, reducing agent volatile matter, and various products of thermal decomposition, rises from the top of the furnace carrying fume and entrained micron-size particles of the charge. In an open furnace all of the carbon monoxide burns with induced air at the top of the charge, resulting in a large volume of high temperature gas. In a closed furnace most of the carbon monoxide is removed without combustion with air. Due to the steady state operation of the submerged arc furnace, gas generation is continuous.

Additional fume is generated at the furnace tapholes, principally the result of air flow induced by heat transfer from the molten metal or slag. After the taphole, there are other sources of fume that occur in handling the metal. Because most furnaces are tapped intermittently, these fumes occur only part of the operating time.

As mentioned above, the fume size is generally below 2 microns; fume chemical analysis from the typical open-type furnace producing ferromanganese shows the manganese oxide content to be

about 33 percent.

In addition to the numerous intermittent and continuous gas flows described, other factors also contribute to the problem of air pollution control. Manganese ores contain volatile matter and moisture that disturb the smooth operation of the furnace. Sudden release of gas results in substantial charge ejection from the furnace.

Normal gas flow from the typical closed furnace producing ferromanganese is approximately 160 to 170 scfm per megawatt and peak flows may be 40 percent higher. From an open furnace with a low hood the gas flow rate may be in the order of 3,000 to 5,000 scfm per megawatt.

Atmospheric emissions resulting from the production of ferromanganese in blast furnaces average 4.1 pounds of manganese per ton based on 95 percent control, 20 percent manganese in the particulate (Table II), and 410 pounds of particulate per ton of ferromanganese (uncontrolled) [1]. During 1968 the manganese emissions totaled 1,113 tons.

Emissions to the atmosphere from electric furnaces producing

1- Office of Air Programs; Emissions report in progress; 1971.

ferromanganese average 23.9 pounds of manganese per ton of ferromanganese produced including a 10 pound per ton loss during handling, mixing, and other non-melting operations [1]. In the United States the manganese emissions from electric furnaces during 1968 totaled 3,669 tons.

Atmospheric emissions due to the production of silicomanganese in electric furnaces averaged 69.4 pounds of manganese per ton including a 10 pound per ton loss during handling, mixing, and other non-melting operations [1]. During 1968 manganese emissions resulting from the production of silicomanganese totaled 4,164 tons.

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1. Office of Air Programs; Reactive metals report in progress; 1971.

REPROCESSING

More than ninety percent of the manganese used in the United States during 1968 was consumed by the steel industry in the production of carbon steel, stainless steel, and special steel alloys, The remainder was used in making cast iron, nonferrous alloys, batteries, chemicals, and numerous other products.

CARBON STEEL

From the standpoint of air pollution, steel mills are very important sources of manganese emissions. The basic steps in the production of steel include the partial removal of impurities when iron ore is reduced to pig iron in the blast furnace., Further purification takes place when pig iron and scrap are converted to steel in an open-hearth, a basic oxygen, or an electric furnace. Other associated operations include ore crushing, materials handling, sintering, pelletizing and scarfing.

Blast Furnace - Commencing with the production of pig iron, manganese is part of each principal ingredient charged into the blast furnace. It is in the iron and manganiferous ore, in the scrap, and in the slag recycled from the steel converter. More manganese enters the iron blast furnace through the small content of manganese in some iron ores than through the deliberate

addition of manganese. The pig iron emerging from the blast furnace contains about 70 percent of the manganese from the charge, and the other 30 percent is in the slag and gases that are byproducts of the reaction.

As the gas leaves the blast furnace, it contains large quantities of particulates averaging about 150 pounds per ton of pig iron [1]; however, it is subsequently cleaned and used as fuel. The gas cleaning is accomplished in two or three stages and the annual overall efficiency is an estimated 97 percent.

During 1968, 140 million tons of net ores and agglomerates were consumed in producing 89 million tons of pig iron [2]. The estimated manganese content of the particulate was 0.5 percent. Emissions to the atmosphere totaled 1,000 tons, based on 22.5 pounds of manganese per 1,000 tons of pig iron.

Open-Hearth Furnace - The next step in steelmaking is to produce steel using pig iron, home scrap, and purchased scrap. Three types of furnaces are commonly used; the open-hearth, the basic oxygen, and the electric furnace. Regardless of the

---

1- "Air Pollutant Emission Factors"; Environmental Protection Agency; Preliminary Document; Apr. 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

kind of furnace, the primary object of the operation is to reduce the impurities present in the charge to the limits specified for the melt.

In the open-hearth furnace, steel is produced from a mixture of scrap (about 45 percent) and pig iron (about 55 percent) using oil, coke-oven gas, natural gas, tar, or producer gas to provide the required heat. The melting begins when the first scrap is charged and continues as solid material is added. After all the scrap has melted, molten pig iron is delivered and poured into the furnace. This step is followed by the ore and lime boil. Next the working period is employed to: (1) lower the phosphorus and sulfur content; (2) eliminate carbon as rapidly as possible; and, (3) increase the heat for final deoxidation. It is during this process that the greatest loss of manganese occurs. About 80 to 90 percent emerges in the fume and slag. It oxidizes readily and tends to pass into the slag, rather than remaining with the product.

The overall operating cycle of the open-hearth furnace is about 10 hours; fumes are discharged continuously at varying rates. In spite of the varying actions, average emission factors have been established for operation both with and without oxygen

lancing. With oxygen lancing, the factor for uncontrolled emissions is 21 pounds of particulate per ton of steel. Without lancing, the factor is 8 pounds per ton. The degree of emission control is estimated at 40 percent, and the average emission factor (controlled) for all open-hearth furnace operations is 10.2 pounds of particulate per ton of steel produced [1].

The mean particle size of the dust is generally considered to be 0.5 micron [2] and a typical chemical analysis is shown in Table III.

During 1968 the steel produced in open-hearth furnaces was 65 million short tons [3], and the manganese content of the particulate matter emitted was about 0.5 percent. Manganese emissions to the atmosphere totaled 1,660 tons based on 51 pounds per 1,000 tons of steel produced.

Basic Oxygen Furnace - The basic oxygen furnace is a refractory-lined, cylindrical vessel that is mounted on trunions so that it can be rotated and placed in a horizontal or vertical

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1- "Emissions, Effluents and Control Practices"; Environmental Protection Agency; Study in progress (unpublished); 1970.

2- Aberlow, E. B.; "Modification to the Fontana Open-Hearth Precipitators"; JAPCA; 7; May, 1957.

3- Minerals Yearbook; Bureau of Mines; 1968.

TABLE III

SPECTROGRAPHIC ANALYSIS OF PARTICULATE DISCHARGE FROM AN OPEN-HEARTH FURNACE [1]

Element	Approximate Amount* Percent
Fe	Remaining amount
Zn	10 to 15
Na	1 to 2
K	1 to 2
Al	5
Ca	5
Cr	2
Ni	2
Pb	5
Si	5
Sn	1
Cu	0.5
Mn	0.5
Mg	0.1
Li	Trace
Ba	Trace
Sr	Trace
Ag	0.05
Mo	Trace
Ti	Trace
V	0.05

*These data are qualitative only and require supplementary quantitative analysis for actual amounts.

1- Air Pollution Engineering Manual; Public Health Service Publication No. 999-AP-40; p. 243; 1968.

position as required during operation. When charged and in the vertical position, a stream of oxygen is supplied from overhead downward into the converter. The oxygen impinges on the liquid metal surface causing violent agitation and intimate mixing with the pig iron. During the operating cycle of about one hour, large quantities of gas and particulate are discharged from the furnace.

The emission factor for the basic oxygen furnace has been estimated at 46 pounds of particulate per ton of steel [1]/ and the degree of emission control at 97 percent. The mean particle size of the dust is 0.7 micron (Table IV).

During 1968 the steel produced in basic oxygen furnaces was 48 million short tons [2]/ and the estimated manganese content of the particulate emissions was 3.2 percent (Mn_3O_4 4.4 percent as shown in Table V). Manganese emissions to the atmosphere totaled 1,060 tons during the year, based on 44 pounds per 1,000 tons of steel produced.

1- "Air Pollutant Emission Factors"; Environmental Protection Agency; Preliminary Document: Apr. 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

TABLE IV

PARTICLE SIZE DISTRIBUTION OF FUME FROM A BASIC OXYGEN FURNACE [1]

Microns	Percent
0 - 0.5	20.0
0.5 - 1.0	65.0
1.0 - 15.0	15.0

TABLE V

COMPOSITION OF FUME AND DUST FROM BASIC OXYGEN FURNACES [1]

Material	Percent
Fe_2O_3	90.0
Mn_3O_4	4.4
FeO	1.5
SiO_2	1.3
CaO_2	0.4
P_2O_5	0.3
Al_2O_3	0.2

1- Gaw, R. G.; "Symposium on Basic Oxygen Furnaces, Gas Cleaning"; Iron Steel Engr.; 37; Oct. 1960.

Electric Furnace - Electric arc furnaces are well suited to the production of alloy steels and are used extensively for that purpose. They are refractory-lined, cylindrical vessels with large carbon electrodes passing through the furnace roof.

Emissions generated during steelmaking consist of fume and dust emitted from the furnace during charging and refining. While charging the furnace, the top is open to receive the cold metal and the exposure of the cold charge to the high temperature inside the furnace results in the generation of large quantities of fume. In general, the rate of fume release increases throughout the operation.

Particulate emissions from electric arc furnaces have been estimated at 11 pounds per ton of steel with oxygen lancing, and 7 pounds per ton without [1]. The particle size is shown in Table VI. The degree of control is estimated at 78 percent, and the average emission factor (controlled) at 2.5 pounds per ton of steel produced.

During 1968 the steel produced in electric arc furnaces was 16 million short tons [2]. The manganese content of the

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1- Air Pollutant Emission Factors; Environmental Protection Agency; Preliminary Document; Apr. 1971.

2- Minerals Yearbook; Bureau of Mines; 1968.

TABLE VI

ELECTRIC ARC STEEL FURNACE
FUME PARTICLE SIZE

Microns	Percent	
	A	B
0 - 5	71.9	67.9
5 - 10	8.3	6.8
10 - 20	6.0	9.8
20 and larger	13.8	15.5

A - Los Angeles County Air Pollution Control District, unpublished data, Los Angeles, California, 1950-51.

B - Erickson, E. O.; "Dust Control of Electric Foundries in Los Angeles Area"; Electric Furnace Steel Process; American Institute of Mining and Metallurgical Engineers; 11; 1953.

particulate emissions is estimated at 3.1 percent (4 percent MnO as shown in Table VII). Manganese emissions to the atmosphere totaled 620 tons, based on 78 pounds per 1,000 tons of steel produced.

OTHER STEEL

Even though there is more manganese in certain alloy steels than in carbon steel, the production steps are essentially the same. The principal difference is that more of the alloying elements are added near the end of the cycle.

Stainless steels are usually produced in an electric arc or high-frequency induction furnace. The largest tonnages are processed in an electric arc furnace of the Heroult type. This furnace is refractory-lined and the steel may be poured by tilting the entire furnace. After the working period the slag is removed and a finishing slag is placed on the bath prior to the addition of manganese and other alloying elements.

Manganese steels are made by any of the conventional steel-making processes with the exception that an acid-lined furnace may not be used. Only a base iron charge is melted in the acid-lined furnace. The ferromanganese or other manganese alloy is melted separately in a basic-lined furnace and added

TABLE VII

TYPICAL EMISSIONS FROM AN ELECTRIC ARC FURNACE [1]

Component	Weight %
Zinc Oxide (ZnO)	37
Iron Oxides	25
Lime (CaO)	6
Manganese Oxide (MnO)	4
Alumina (Al_2O_3)	3
Sulfur Trioxide (SO_3)	3
Silica (SiO_2)	2
Magnesium Oxide (MgO)	2
Copper Oxide (CuO)	0.2
Phosphorus Pentoxide (P_2O_5)	0.2

1- Coulter, R. S.; "Smoke, Dust, Fumes Closely Controlled in Electrode Furnaces"; Iron Age; 173; Jan. 14, 1954.

to the base iron in the ladle. Hadfield's method consists of adding molten ferromanganese to carbon-free blown iron. This is the most widely used method for producing manganese steel castings.

Manganese emissions resulting from the production of alloy steels have been included with the emissions estimated for carbon steel.

CAST IRON

The principal use of manganese in cast iron is to nullify the effects of sulfur. In spite of recent advancements in the technology of melting with electric arc and induction furnaces, the cupola is still the most widely used method for producing cast iron. The charge into the cupola furnace includes coke, scrap, and pig iron, each containing some manganese. As air is introduced, the coke burns and causes the metallic charge in the furnace to melt. Part of the manganese oxidizes and part combines with sulfur to form manganese sulfide which is discharged in the slag.

The rate of particulate emissions from gray iron cupolas has been reported as 4 to 26 pounds per ton of process weight not including emissions from handling, charging, or other non-melting operations.

Based on information obtained from industry the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The manganese content of the particulate is 2 percent [1]/ and the degree of emission control approximately 25 percent.

During 1968 the pig iron and scrap used by iron foundries totaled 16,788,000 short tons [2]/. Manganese emissions to the atmosphere due to the production of cast iron were 2,770 tons.

WELDING RODS

Some welding rods and welding rod coatings contain manganese. In the coatings there is approximately 10 percent manganese dioxide as shown in Table VIII, and in aluminum welding rods there is as much as 1.5 percent manganese.

During the production of aluminum welding rods the manganese is added as a general purpose alloy for applications requiring moderate strength and good workability. An aluminum-rich alloy ingot containing the manganese is added to a charge of

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1- Private communication with industrual source.

2- Minerals Yearbook; Bureau of Mines; 1968.

TABLE VIII

TYPICAL ANALYSIS OF WELDING ROD COATINGS

Material	Percent
SiO_2	20.5
TiO_2	41.5
MnO_2	10.9
Fe_2O_3	8.8
MgO	5.9
CaO	2.5
CO_2	1.4
Moisture, organic volatile matter	6.9
Other	1.6
TOTAL	100.0

virgin aluminum and alloy scrap in a reverberatory furnace fired to a temperature of about 1,400 F. During the melting process the metal flows from the main furnace hearth to the holding hearth through a trough outside the furnace enclosure. The metal is then tapped and poured into ingots and cooled.

Next, the ingots are heated and rolled in the blooming mill prior to milling in the rod mill. The product is finished by forging, swaging, or drawbenching.

Based on information obtained from three industrial sources, manganese emissions to the atmosphere are estimated at 16 pounds per ton of manganese processed. During 1968 the manganese emissions resulting from the manufacture of welding rods totaled 24 tons.

NONFERROUS ALLOYS

In aluminum alloy production, manganese is dissolved in the molten aluminum to provide superior hardness, tensile strength, and corrosion resistance. Such alloys contain manganese at a level of less than 25 percent; one master alloy uses 4 or 5 percent.

Magnesium producers use manganese chloride as a flux to impart qualities of stiffness, hardness, and corrosion resistance.

Also, magnesium can be melted and alloyed in steel pots when manganese is used since it inhibits alloying of the magnesium with the steel.

When alloyed with copper and zinc, manganese bronze is formed. These bronzes, containing up to 3.5 percent manganese, possess good tensile strength and are well known for their resistance to the corrosive effects of sea water.

Manganese-copper-nickel alloys have a high affinity for carbon and rapidly attack acid refractories. Therefore, melting should be conducted in a basic-lined high-frequency furnace. The basis of the furnace charge consists of ordinary carbon-free metallic manganese, ingot copper, nickel pellets, and returned scrap from previous melts, if available. Satisfactory results have been obtained by melting the copper and nickel under an oxidizing slag of manganese ore.

Producers of nonferrous alloys contacted during this study stated their atmospheric emissions average about 12 pounds per ton of manganese processed. During 1968 manganese emissions to the atmosphere were 60 tons.

BATTERIES

An important use of manganese dioxide is as a depolarizing agent in the ordinary dry cell battery. Hydrogen released from the electrolyte of the cell tends to form around the carbon electrode, slowing the action of the cell. This condition is corrected as the hydrogen combines with the oxygen that is provided by manganese dioxide contained in the cell mix.

The main steps in a dry cell battery-making process are diagramed in Figure II.

Emissions to the atmosphere are principally during the early stages of production. Manganese dioxide, calcined manganese, and other dry ingredients are emptied from vats and containers into a dry mixer. These mixed ingredients then travel in bucket elevators to the hopper where they are dumped and enter the wet mixer.

Information obtained from manufacturers of dry cell batteries shows that their manganese emissions to the atmosphere average 10 pounds per ton of manganese processed. During 1968 the atmospheric emissions were 90 tons.

FLOW DIAGRAM

BATTERY MANUFACTURING

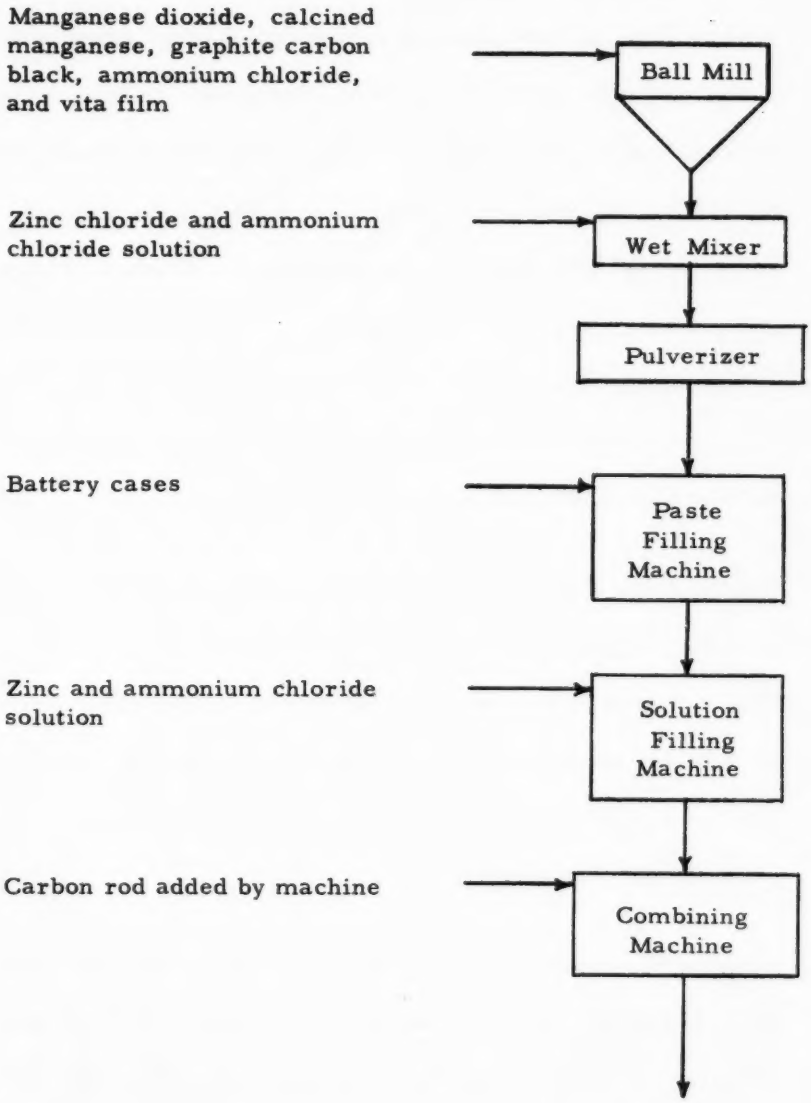

Figure II

CHEMICALS AND OTHER USES

Manganese ore, mainly in dioxide form, is used in the chemical industry as an oxidizing agent in the manufacture of hydroquinone and for the production of various manganese chemicals, including potassium permanganate, manganese sulfate, manganous chloride, and manganous oxide. It is used in the leaching of uranium and zinc ores, in fertilizers as a trace element, in animal and poultry feed as a supplement, in pharmaceuticals, frits, glass, ceramics, and to give a variety of coloring effects to face brick. For certain of these applications the ore is used directly; for others, it may be processed into compounds or salts of manganese prior to use in the final product.

Hydroquinone is important as a photographic developer. Permanganates have many uses in a wide variety of applications. They are used in the chemical industry in air pollution control for sulfides and mercaptans, in water treatment, as bactericides and pesticides, and for odor control in barnyards. Potassium permanganate is a powerful oxidant.

Manganese sulfate is used in a multitude of commercial products; one of the largest areas is as a fertilizer or fertilizer additive. It is also important as a constituent of animal and

poultry feeds, fungicides, paint driers, coloring agents for the textile and ceramic industries, and is often used as a base for the production of other manganese chemicals. Approximately 10,000 tons of manganese are used annually in the production of fertilizers.

Manganous oxide is also found in fertilizers and in animal and poultry feeds. In addition it is used in certain welding applications. In dyeing textiles, making welding rod fluxes, and in alloying manganese with magnesium, manufacturers use manganous chloride.

Another area of interest is the molybdenum-manganese process of joining ceramics to metal, better known as the moly-manganese process. It is one of the most widely employed methods in electronic applications. A thin coating (0.005 to 0.002 inch) of a fine suspension of molybdenum and manganese is fired on the ceramic in a reducing atmosphere at temperatures approaching 3,000 F. Then a coating of nickel and copper is electroplated over the molybdenum and manganese, and is wetted by a brazing alloy. The resulting metal-ceramic bonds have a better high-temperature strength than those formed by any other method. Tensile strength of 20,000 pounds per square inch has been reported.

Fuel additives of organic manganese compounds have been patented and tested. The most successful antiknock compound is methylcyclopentadienyl manganese tricarbonyl, which is mixed with tetraethyl lead to increase the octane rating of gasoline. A typical mixture is composed of the following ingredients: 57.5 percent tetraethyl lead; 7.0 percent methylcyclopentadienyl manganese tricarbonyl; 16.7 percent ethylene dibromide; 17.6 percent ethylene dichloride; and 1.2 percent other additives such as dye and inert materials.

Various methods of using manganese to remove air pollutants have been suggested. Manganese nodules from the ocean floor can be loosely packed in a column through which a gas passes, causing a reaction with the sulfur dioxide in the gas to produce manganese sulfate. One-third of the manganese can be recovered from the sulfated nodules by leaching with weak sulfuric acid.

There is no reliable information regarding the average manganese emissions that occur during the production of compounds and the subsequent manufacture of products that contain manganese. However, a few rough estimates of atmospheric emissions have been obtained from people in industry. In this report

manganese emissions to the atmosphere are 10 pounds per ton of manganese processed.

During 1968 the manganese in chemicals and other miscellaneous uses was 60,000 tons, and atmospheric emissions were an estimated 300 tons.

CONSUMPTIVE USES

The largest manganese emissions to the atmosphere during consumptive use are those due to the combustion of coal and oil. Others that occur are usually of such a nature that atmospheric emissions are negligible.

COAL

The manganese content of various samples of coal has been reported as shown in Table IX, and the average concentration in domestic coal is about 26.4 ppm. Coal consumed in the United States during 1968 was 508,990,000 tons (bituminous and anthracite) [1]; therefore, the manganese in coal was about 13,400 tons. Since fly ash is about 65 percent of total ash and approximately 75 percent of fly ash is collected, the manganese emissions to the atmosphere should be 16 percent of the manganese contained in the coal, or 2,150 tons.

A study has been made regarding emissions from coal fired power plants and the emissions of manganese have been recorded. Six power boilers were tested, each a different type, and each value reported was the average of at least two tests. Two of

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1- Minerals Yearbook; Bureau of Mines; 1968.

TABLE IX

AVERAGE MANGANESE CONTENT IN ASH OF COAL

Region	Frequency of Detection - %	Mn Content of Ash - %	Ash Content of Coal - %	Mn Content of Coal -%
Eastern Province	100	0.026	9.3	0.0024
Interior Province	100	0.0325	10.5	0.0034
Western States	100	0.0212	9.8	0.0021
Average Manganese Content of Coal				0.00264

NOTE - The above table based on "Spectrochemical Analyses of Coal Ash for Trace Elements" Table 1; Bureau of Mines RI 7281; July, 1969.

the boilers were fired with Illinois coal; two burned Pennsylvania coal; one used some coal from Ohio and some from West Virginia; one burned part Kentucky and part West Virginia coal.

Manganese concentrations in the fly ash samples taken before fly ash collection ranged from 4.2 to 17.0 grains per scf x 10^{-4}. The average was 8.47 grains per scf x 10^{-4}. In the samples taken after fly ash collection, the manganese concentration ranged from 0.26 to 1.6 grains per scf x 10^{-4} and the average was 0.92 grains per scf x 10^{-4} [1]. Based on 508,990,000 tons of coal consumed in the United States during 1968, 90 percent application of control, 160 scf of flue gas per pound of coal and the average concentration in fly ash stated above, the manganese emissions for 1968 due to the combustion of coal are calculated at 1,950 tons.

$$\frac{508,990,000 \times 160 \times 2,000}{7,000 \times 2,000}\left[(0.92 \times 10^{-4} \times 0.9) + (8.47 \times 10^{-4} \times 0.1)\right] = 1,950$$

In this report the figure of 1,950 tons is used as manganese emissions to the atmosphere due to the combustion of coal.

1- Cuffe, Stanley T. and Gerstle, Richard W.; "Emissions from Coal Fired Power Plants"; Public Health Service Publication No. 999-AP-35; 1967.

OIL

In order to estimate manganese emissions to the atmosphere resulting from the combustion of fuel oil, it was necessary to determine the manganese content as well as the quantity of oil received from numerous foreign and domestic sources. Analyses of more than 400 samples of crude and residual oils were obtained from the major oil companies and the utilities along the east coast of the United States.

The data show that nearly all crude oil contains some manganese; the concentrations ranging from nearly zero to more than 2,000 ppm. It also shows that residual oil contains a higher percentage of manganese than the crude. When oil is refined the manganese and other trace metals tend to concentrate in the heavy fractions; the residual oil, the road oil, and the asphalt. According to the information obtained from oil companies, the residual fuel oils may be expected to contain 4 to 6 times as much manganese as the crude oils.

Unfortunately, most of the analyses available were of crude oil. They show oil from California, Colorado, and Utah contains more manganese than that from Kansas, Oklahoma, and Texas (Table X). Residual fuel oil from the United States contains about 158 ppb manganese, while that from the Middle East

TABLE X

MANGANESE CONTENT OF DOMESTIC CRUDE OILS

Source	Manganese Content - ppb
Arkansas	120
California	138
Colorado	208
Kansas	13
Montana	5
New Mexico	21
Oklahoma	30
Texas	29
Utah	1,445
Wyoming	44

NOTE - The above table is based on private communication with industrial sources.

averages about 120 ppb. Analyses of eight residual fuel oils from South America show that manganese is below the limit of detection.

During 1968 the demand for residual fuel oil in the United States was 668,239,000 barrels. Imports were 409,928,000 barrels, and the remainder were principally from domestic production 1/. Imports were about 92 percent from South America and the West Indies; 8 percent from the Middle East, Canada, and other countries 2/.

MANGANESE IN RESIDUAL OIL
CONSUMED IN THE UNITED STATES - 1968

Source	Quantity Barrels	Mn Content ppb	Mn Content Tons
United States	258,311,000	158	7
South America	376,000,000	-	-
Middle East and Other	33,928,000	120	1
TOTAL	668,239,000		8

1- "Crude Petroleum, Petroleum Products, and Natural-Gas-Liquids: 1968"; Petroleum Statement, Annual; Mineral Industry Surveys; Bureau of Mines; Washington, D.C.

2- Based on import data from the Office of Air Programs; Durham, N.C.

In the past power boilers designed to burn fuel oil were not usually equipped with air pollution control apparatus. It was only the coal fired or the combination coal-oil units that included mechanical collectors and/or electrostatic precipitators. When these combination units burn oil, only a small part of the particulate matter becomes an atmospheric emission.

The records show that 669 million barrels of residual oil were consumed in the United States during 1968. The electric utilities used 28 percent of the total, or 185 million barrels, and were the only users with any significant degree of air pollution control. A survey was conducted and it was determined that the electric utility percent of control when burning fuel oil was about 32 percent.

Based on 10 percent overall control, the manganese emissions to the atmosphere during 1968 due to the combustion of fuel oil totaled 7 tons.

INCINERATION AND OTHER DISPOSAL

Information concerning sewage and sludge was the only data available during this study regarding atmospheric emissions of manganese that result from incineration or disposal.

SEWAGE AND SLUDGE

A recent report concerning the burning of sewage and sludge indicates the present burning rate in the United States is about 2,000 tons per day [1]. Based on a manganese content of 240 ppm (dry weight) [2] the atmospheric emissions currently total 175 tons of manganese per year.

1- Private communication from the Federal Water Pollution Control Authority.

2- Clark, L. J. and Hill, W. L.; "Occurrence of Manganese, Copper, Zinc, Molybdenum, and Cobalt in Phosphate Fertilizers and Sewage Sludge"; J. Assoc. Official Agr. Chemists; 41; pp. 631-637; 1958.

APPENDIX A

COMPANIES DEALING IN MANGANESE AND MANGANESE COMPOUNDS

ALABAMA	LOCATION
Woodward Company	Woodward
CALIFORNIA	
American Potash and Chemical Corp.	Los Angeles
Capco Alloy Steel Company	Los Angeles
Electronic Space Products, Inc.	Los Angeles
Metal Organics, Inc.	San Carlos
Wilson and George Meyer & Company	So. San Francisco
Mountain Copper Company, Ltd.	Martinez
CONNECTICUT	
Anaconda American Brass Company	Waterbury
Michael Schiavone & Sons, Inc.	New Haven
D. C.	
Hercules, Inc.	Washington
GEORGIA	
Frank Smith	Cartersville
Tennessee Corporation	Atlanta
ILLINOIS	
Amsco Division of Abex Corp.	Chicago Heights
Atlantic Chemicals and Metals Co.	Chicago
Carus Chemical Company	LaSalle
Ben J. Harris and Company	Chicago Heights
Hickman, Williams and Company	Chicago
Kraft Chemical Company	Chicago

R. Lavin and Sons, Inc.	Chicago
Miller and Company	Chicago
Stresen-Reuter International	Bensonville
Wilson Labs	Chicago

IOWA

Bonewitz Laboratories, Inc.	Burlington

MARYLAND

Ansam Metals Corporation	Baltimore
Chemetals Division, Diamond Shamrock Chemical Company	Baltimore
Glidden Metals Group	Baltimore
Manganese Chemical Corporation	Baltimore

MICHIGAN

Frankel Company, Inc.	Detroit
Haviland Products Company	Grand Rapids

MINNESOTA

Manganese Chemical Corporation	Minneapolis

MISSOURI

Mallinckrodt Chemical Works	St. Louis

NEW JERSEY

Advance Division, Carlisle Chemical Works, Inc.	New Brunswick
A and S Corporation	Verona
J. T. Baker Chemical Company	Phillipsburg
Leonard J. Buck, Inc.	Jersey City
Eastern Chemical Corporation	Pequannock

General Metallic Oxides Company	Jersey City
Hummel Chemical Company, Inc.	Newark
Import Chemical Company	Jersey City
Metallurgical International Inc.	New Shrewsbury
Nitine, Inc.	Whippany
Octagon Process, Inc.	Edgewater
Shieldalloy Corporation	Newfield
Taylor-Wharton Company	High Bridge
Tenneco Chemicals, Inc.	Piscataway
Troy Chemical Corporation	Newark
Var-Lac-Oid Chemical Company	Elizabeth
Max Zuckerman and Sons, Inc.	Owings Mills

NEW YORK

Airco Alloys and Carbide Division	Niagara Falls
Air Reduction Company, Inc.	New York
Allied Chemical Corporation	New York
Alloys Unlimited, Inc.	Melville
American Smelting and Refining Co.	New York
Anchor Metal Company, Inc.	Brooklyn
Anglo-American Metal & Ferro Alloy Corporation	New York
Associated Metals and Minerals Corp.	New York
Atomergic Chemetals Company	Carle Place, L.I.
H. J. Baker Brothers, Inc.	New York
Belmont Smelting & Refining Works, Inc.	Brooklyn
Berkshire Chemicals, Inc.	New York
Charles B. Chrystal Company, Inc.	New York
City Chemical Corporation	New York
Cometals, Inc.	New York
Continental Ore Corporation	New York
Debevoise-Anderson Company, Inc.	New York
Faesy and Besthoff, Inc.	New York
Fallek Products Company, Inc.	New York
Gallard-Schlesinger Chemical Manufacturing Corporation	Carle Place, L.I.
M. Golodetz and Company	New York
W. R. Grace and Company	New York
Herzog Metal Corporation	New York
Hooker Chemical Corporation	Niagara Falls
Industrial Chemical and Dye Corp.	New York
A. Johnson and Company, Inc.	New York
Kingston Chemical Company, Inc.	New York

Kolon Trading Company, Inc.	New York
Mackenzie Chemical Works	Central Islip
McKesson Chemical Company	New York
Messina, Inc.	Bedford Hills
Metallurg Alloy Corporation	New York
Milwaukee Tool and Equipment Co.	New York
Wm. H. Muller and Company, Inc.	New York
Naftone, Inc.	New York
The New Jersey Zinc Company	New York
Ore and Ferro Corporation	New York
Pancoast International Corporation	New York
Charles Pfizer and Company, Inc.	New York
Philipp Brothers	New York
Primary Industries Corporation	New York
Progressive Alloys Corporation	Brooklyn
The Selney Company, Inc.	New York
Semi Alloys, Inc.	Mount Vernon
E. M. Sergeant Pulp and Chemical Company, Inc.	New York
Smith Chemical and Color Co., Inc.	Brooklyn
Sterwin Chemicals, Inc.	New York
C. Tennant Sons and Company	New York
The Titan Industrial Corporation	New York
Union Carbide Corporation, Ferro-alloys Division	New York
Union Carbide Corporation, Mining and Metals Division	New York
United Mineral and Chemical Corp.	New York
Winthrop Laboratories	New York
Witco Chemical Corporation	New York

NORTH CAROLINA

Mineral Research and Development Corp.	Concord

OHIO

Barium and Chemicals, Inc.	Steubenville
Chemetron Corporation	Cleveland
Chemical Division Ferro Corporation	Bedford
Glidden-Durkee Division	Cleveland
Globe Metallurgical Division, Interlake Steel Corporation	Cleveland

Haley Smelting, Inc.	Parma
Hall Chemical Company	Wickliffe
Harshaw Chemical Company	Cleveland
McGean Chemical Company	Cleveland
Mooney Chemicals, Inc,	Cleveland
Oglebay-Norton Company	Cleveland
Ohio Ferro-Alloy Corporation	Canton
Pickards Mather and Company	Cleveland
I. Schumann and Company	Bedford
S. C. M. Corporation	Cleveland
Shepherd Chemical Company	Cincinnati
C. L. Zimmerman Company	Cincinnati

PENNSYLVANIA

Bethlehem Steel Corporation	Bethlehem
Bram Metallurgical Chemical Co.	Philadelphia
Brass and Copper Sales, Inc.	Philadelphia
C. E. Minerals	King of Prussia
Ceramic Color and Chemical Manufacturing Company	New Brighton
Chase Chemical Corporation	Pittsburgh
Chemalloy Company, Inc.	Bryn Mawr
Chromium Mining and Smelting Corp.	Pittsburgh
Colonial Metals Company	Columbia
Damascus Steel Casting	New Brighton
Fisher Scientific Company	Pittsburgh
Foote Mineral Company	Exton
Gano Moore Company, Inc.	Wynnewood
O. Hommel Company	Pittsburgh
Lavino Division, International Minerals and Chemicals Corp.	Philadelphia
Mercer Alloys	Greenville
Metallurgical Products Company	Philadelphia
J. Meyer and Sons, Inc.	Philadelphia
Prince Manufacturing Company	Bowmanstown
Reading Alloys, Inc.	Robesonia
Frank Samuel and Company, Inc.	King of Prussia
Shenango, Inc.	Pittsburgh
Taylor-Wharton Company, Division of Harsco Corporation	Easton
Charles A. Wagner Company, Inc.	Philadelphia
Welding Wholesale Company	Philadelphia

TENNESSEE

Eastman Chemical Products, Inc.	Kingsport
Foote Mineral Company	Knoxville

(American Metal Market, Aug. 10, 1970; Thomas Register, Dec. 1968 Ed.)